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(54) y Title of the Invention z Method of producing ethyl acetate and its production apparatus

(57) y Summary z

yPurpose zTo establish a method and a production apparatus stated above for obtaining ethyl acetate by adopting a reaction between ethylene and acetic acid in gas state in order to control any possible side reaction, so that the ethyl ace can be collected with high efficiency and high yield in addition to cost effectiveness as well as easy maintenance.

yStructure z Gas mixture of ethylene and acetic acid(1) in gas state goes through and reacts with at least two insu layers of catalysts(4),(14), (24) in series, comprising of heteropolyacid or heteropolyacid salts. A cooling unit (3) or (13) set between any two adjacent insulated layers of catalysts (4-14 or 14-24) to cool down oncoming gas mixture w temperature has been raised by reaction heat at the previous stage before proceeding to the next.

y The Extent of the Patent Claim z

insulated layers of catalysts to cool it down before proceeding to the next stage.

yClaim 2 zA method to produce ethyl acetate that features a cooling unit which cools down the gas mixture while ensuring the temperature rise by the reaction stays within 30 maximum inside the insulated layers of catalysts at later stages when applying the method stated in Claim 1.

yClaim 3 zAn apparatus for producing ethyl acetate which consists of insulated reactors with at least two insulated layer of catalysts in series comprising of heteropolyacid or heteropolyacid salts that lead the gas mixture of ethylene and acetic acid flow and react, and cooling systems inserted between these adjacent insulated reactors to cool down oncoming gas mixture whose temperature has been raised by reaction heat at the previous stage.

yClaim 4 z With relation to the apparatus for producing ethyl acetate stated in Claim 3, an apparatus for producing ethyl acetate with the above cooling system which enables the temperature rise of the gas mixture on exiting the later stage to stay within 30 maximum inside the insulated reactor.

y Detailed Explanation on the Invention z

y 0001 z

yPossible Application in the Industrial Field zThis invention concerns method and apparatus for producing ethyl acetate especially a method that produces ethyl acetate with high yield and high efficiency by means of addition reaction with ethylene and acetic acid in the presence of catalysts, and an reaction apparatus dedicated to this production method.

y 0002 z

yUsual Method zThe inventors concerned had submitted a method to produce ethyl acetate with high yield by means addition reaction in gas state with ethylene and acetic acid in the presence of solid catalysts (see Official Report No. Tok Kai-Hei 4-139149). This method involves a process in which ethylene and acetic acid are contacted with solid catalys comprised of heteropolyacid or heteropolyacid salts. However in general, if this method is enforced in the industry. isotherm reaction apparatus using shell-tube reactor as shown in Figure 2 is usually adopted. Figure 2 shows one example isotherm reaction apparatus and consists of heating system(2) which heats up the gas mixture of ethylene and acetic acid a suitable starting temperature, and shell-tube reactor(30) which helps the heated gas mixture(1) contact and react with solid catalysts. The structure of this shell-tube reactor(30) contains a multiple tube thermal interchange device. Inside group of tubes(40) in parallel filled with granular solid catalysts. The gas mixture(1) flows from one end of these tubes to the other end, thus new gas(50) flows out after the contact reaction inside the tubes. The contact reaction betw ethylene and acetic acid is an exothermic one, therefore each tube in the group of tubes(40) is cooled down by cool medium(6) from outside in order to remove reaction heat and keep the temperature of the system constant, thus an ic reaction temperature is maintained.

y 0003 z

yThe problem this invention tries to overcome zSince the above shell-tube reactor(30) is complicated in structure expensive to set up, a more simply structured apparatus was sought after. The tubes inside the shell-tube reactor designed in a long and skinny shape to enhance the efficiency of heat exchange. On the other hand, in such cases of co reaction, they are also prone to continuous condensation caused by the catalysts during the operation, which undermine catalyst activity as well as preventing the gas to flow smoothly and consequently this declines space velocity that resul the necessity to change catalysts after regular operating cycles. The labour and time consumed for removing the dam and the inside of the long and skinny tubes results in a huge expense of maintaining the appar

has a single tube, which makes the structure simple and inexpensive, on top of that, it is easier to remove the damaged catalysts. But if the normal method is used for the insulated reactor, it will not be able to control the catalysts inside the reactor, which will result in an overheated condition that would cause an undesirable side reaction such as polymerisation or decomposition of ethylene which would not only decrease the conversion rate to ethyl acetate, but also undermine the activity of the catalysts because of the presence of carbon matter on the catalysts. This could even promote the side reaction further by provoking "uncontrollable reaction". For these reasons, this method is concluded to be unacceptable. The invention took place in order to solve these problems and its purpose was set to provide a method that would ultimately produce ethyl acetate with high yield and high efficiency using an insulated reactor, and an apparatus dedicated to this method.

y 0005 z

yThe measures taken to solve these problems zThe above problems can be solved by providing a method of producing ethyl acetate which flows out after the original gas mixture of ethylene and acetic acid flows through and reacts with at least two insulated layers of catalysts and is cooled down by a cooling unit set between two adjacent insulated layers of catalysts as reaction heat generates at each stage. In this procedure, the ideal thing is to cool down the gas mixture at the cooling unit to ensure the reaction heat rise at later insulated catalysts will stay within 30 maximum. For this reaction, it is also ideal to adjust the space velocity of flowing gas mixture to obtain a total conversion rate to ethyl acetate of 50 to 90% at each insulated layer of catalysts. This invention is to provide an apparatus to produce ethyl acetate and consists of at least two insulated reactors in series containing insulated layers of catalysts which react to the oncoming gas mixture stated above. and cooling systems set between any two adjacent insulated reactors to cool down the gas mixture whose temperature has been raised by the reaction heat generated at the previous insulated reactor. This cooling system is ideally equipped with a facility of suppressing the temperature rise at the exit of subsequent insulated reactor to be within 30 maximum. This production apparatus is also ideally to have a means to adjust the space velocity of the flowing gas mixture to obtain a total conversion rate to ethyl acetate of 50 to 90% at each insulated reactor.

y 0006 z

yFunctioning zSince the contact addition reaction of ethylene and acetic acid is exothermic, it is not very advisable to yield ethyl acetate with a practical conversion rate in mind by using ordinary insulated layers of catalysts. This results in gradual rise of temperature in the system, followed by a side reaction or uncontrollable reaction should the temperature go beyond the tolerance limit. However, by dividing the required amount of insulated layers of catalysts into appropriate portions towards the direction of the gas flow and by setting a cooling system, the gas mixture with risen temperature by reaction heat at the previous layers of catalysts will be cooled down in the middle part of two reactors. In doing so, the reaction heat generated by addition will be kept to a minimum and it will prevent any possibility for temperature in the system as a whole to rise well beyond the tolerance limit.

y0007 z At the system above, to prevent the temperature rise at later insulated layers of catalysts to overheat, it will be better to control the temperature of the gas mixture at the entrance to the catalysts. It is now understood that if the temperature at the insulated layers of catalysts rises by more than 30 , some undesirable consequences such as side reaction, deposition of carbon matter and uncontrollable reaction will follow. Therefore cooling the gas mixture at the cooling unit to keep the temperature rise to stay within 30 will certainly contribute to the increase of conversion to ethyl acetate.

maintaining an ideal constant temperature range for the overall reactor system.

y0009 zNext, with the aid of the diagram, let us explain in more detail about the method of producing ethyl acetate this invention refers to. Figure 1 shows one enforced example of the apparatus for this invention. This particular apparatus for producing ethyl acetate consists of heating system(2) which heats up the gas mixture(1) of ethylene and acetic acid to a temperature required for early stage reaction and then introduces it to the insulated reaction system, three insulated reactors(3), (13) and (23) in series, and cooling systems(12) and (22) which are each inserted between two adjacent insulated reactors (3-13)(13-23). Each of these reactors is composed of insulated layers of catalysts(4), (14), or (24) containing solid catalysts comprised of heteropolyacid or heteropolyacid salts, which will lead the gas mixture(1) to react. The cooling systems(12) and (22) undertake the role of cooling the gas mixture with risen temperature by the reaction heat at the previous stage of insulated reactor(3) or (13).

y0010 zNow let us outline the enforced example of this method of producing ethyl acetate by using the apparatu described above. First of all, supply the gas mixture(1) of ethylene and acetic acid to the heating system(2). The heating system(2) heats up the gas mixture(1) to a temperature (early stage temperature) that enables the reaction to start smoothly in the presence of catalysts. The heated gas mixture is introduced to the first insulated reactor(3). Since this reactor i composed of layers of catalysts(4) filled with solid catalysts comprised of heteropolyacid or heteropolyacid salts, some par of the gas mixture reacts here and converts to ethyl acetate at the same time giving out heat which subsequently raises th temperature higher than the early stage temperature. The new gas mixture(5) that comes out with higher temperature i cooled down by the cooling system(12) which was set between two adjacent insulated layers of catalysts(4-14). The coole gas continues its way to the next insulated layers of catalysts(14), at which more ethylene and acetic acid convert to eth acetate. The new gas mixture(15) that comes out of the insulated layers of catalysts(14) where temperature rise is aga cooled down at the cooling system(22) which was set between two adjacent insulated layers of catalysts(14-24). This gas then led to the following insulated layers of catalysts(24) and likewise more unreacted ethylene and acetic acid a converted to ethyl acetate here, thus new gas compound (25) is collected.

y0011 zNo particular formula in producing the ingredients, ethylene and acetic acid, is specified for this method of invention. To maintain the activity of the catalysts, some vapour are ideally added to the gas mixture(1), although ace acid in a gas state naturally contains some vapour. The ideal amount of supply for the gas mixture to introduce to apparatus of the invention is 1000 2800 / hour at Space Velocity rate with respect to the total contents of catalysts wit the apparatus, with 1400 2300 / hour being ideal. The pressure for this apparatus is selected on the basis that the gas in system remains in a state of gas with some degree of vapour present and yet enough reaction temperature and reaction spe are achieved. Generally, between 5 and 12 atm is considered to be adequate for the operation. The suitable early st temperature to heat up the gas mixture(1) at the heating system(2) is around 130 170 . With temperature bel 130 . the reaction at the insulated reactor(3) does not progress satisfactory, while the temperature beyond 17 increases the chances of side reactions and this should be avoided.

y0012 zThe insulated layers of catalysts(4), (14) and (24) are filled with solid catalysts comprising of heteropolyac heteropolyacid salts. For the examples of heteropolyacid, phosphoric molybdenous acid, phosphoric tungstic acid and tungstic acid can be suitable, while for heteropolyacid salts, cesium salts from phosphoric molybdenous acid, phosph tungstic acid and silic tungstic acid, rubidium salts, thallium salts, ammonium salts and potassium salts, or combinatio these can be used. In fact, heteropolyacid salts mentioned above are to be recommended. The shape of catalysts to be

sphere shape and pushed out shape are especially suitable.

y0013 zAt the cooling unit (cooling systems 12 and 22), the gas mixture should be cooled down so that the reactio temperature at the following insulated layers of catalysts (14 and 24 respectively) would rise by no more than 30 maximum. This can be achieved by adjusting the temperature of flowing gas from each cooling system to stay between 140 and 180 under the above condition of reaction. With temperature below 140 , the conversion rate to ethyl acetate decreases remarkably, on the other hand if the temperature goes beyond 180 , the reaction at insulated layers o catalysts escalates which results in temperature rise of more than 30 at the exit. This could not only induce th possibility of a sharp rise in temperature because of the so-called uncontrollable reaction by catalysts, but also th occurrence ratio of expected ethyl alcohol at the exit of insulated layers of catalysts for example could become 1.5 time more than that at the entrance to the catalysts.

y0014 zIt is ideal for all the insulated layers of catalysts(4), (14) and (24) to have the same composition in terms of i function as a medium to form ethyl acetate by reacting ethylene and acetic acid. The choice of structure, shape, types o solid catalysts comprising of heteropolyacid or heteropolyacid salts, amount of filling, density of filling, whether or nc other substances are included in the filling, space velocity with respect to the supply gas and starting temperature fc reaction can be uniform or different.

y0015 zAt the example shown, three insulated reactors are held in line. Although two reactors might be sufficient, thr to five are preferred. How many reactors are needed is decided by taking into account the degree of the temperature rise each insulated layers of catalysts(4), (14), (24), ... and the temperature of gas at each cooling unit (cooling systems 12, 2 ...), by maintaining a required range of constant temperature in overall insulated layers of catalysts and by assurir 50 ` 90% of the conversion ratio to ethyl acetate at the specified space velocity rate throughout the whole apparatus.

y0016 zAlthough the ratio of conversion to ethyl acetate at each of insulated layers of catalysts(4), (14), (24), ...is limited particularly, equalisation will not only make it easier to control, but also suppress any side reaction to achie:e hi total ratio of conversion. Adjusting the space velocity rate are desired to obtain 50 90% of the total conversion ratic in t apparatus. Generally higher conversion ratio is preferred, but not higher than 90% because the reaction speed slows do under such condition, as well as STY of ethyl acetate decreases as anti-reaction develops, for which an extremely v amount of catalysts will be required to supplement. From this point of view, the conversion rate of around 70% is regarc as most suitable. This ratio can be achieved in the specified apparatus of this invention by controlling the SV rate.

y0017 zAt the above apparatus of producing ethyl acetate, no shape is specified for those insulated reactors (3), ((23),... containing insulated layers of catalysts. However, they are recommended to be cylinder shaped with its insulated wall, one end as an entrance for the gas, the other end as an exit for the flowing gas, in addition, insulated layer catalysts are located in the centre of the cylinder. The layers of catalysts are ideally filled with sediments of catal supported by easily removable devices at both ends so that the exchange of catalysts can be carried out with relative e The insulated reactors can be placed vertically or horizontally, however vertical placement probably will be m advantageous as it require less area for the setting.

y0018 zThe form of cooling systems(12), (22),... to be used for this apparatus can be any of the following: double multiple tubes, spiral tube, tube with fins, layer style or ordinary gas heat exchangers. As for the cooling medium, any o water, oil or medium with volatility can be used provided it serves the purpose of cooling the passing gases down to temperature required. Instead of using a detached cooling system, a different kind of cooling unit can be accommodate

the insulated layers of catalysts to be filled in one long, skinny insulated reactor into two, one in front and one at the back, then place multiple tubes or else a styled cooling system to the middle part of the insulated reactor. However, this will generate condensation of acetic acid and water at the walls where heat exchange is performed, impairing the catalysts through contact. This suggests the cooling unit had better stand independently as a cooling system detached from the insulated reactor. With regard to the temperature of the cooling medium, it is ideally set above the dew point of the in-flow gas mixture. If pressure warm water is used for a cooling medium, it not only overcomes this aspect, but it has the advantage of collecting the vapour generated from the heat exchange process.

y0019 zThe means to adjust SV rate to ensure the total conversion ratio to ethyl acetate to be 50 90% ideally consists of a measuring instrument which continuously measures the temperature at both entrance and exit of each insulated reactor of this production apparatus and the concentration of ethyl acetate in the gas mixture at the exit during the whole operation, plus a control mechanism which controls the temperature at the exit of cooling unit to ensure the concentration set is maintained at the exit of the final insulated reactor as well as automatically controls the speed of flowing gas through overall apparatus.

y 0020 z

y Example enforced z This section describes an enforced example for this invention.

(Apparatus used for experiment) An apparatus of producing ethyl acetate, vertically connecting three long tubes with inner diameter of 24mm as reactors. These reactors shall be called the first reactor, the second reactor and the third reactor in parallel with the direction of the flow that the reacted gas will travel. On the top of these reactors, temperature adjusting units are equipped and some catalysts are filled below them to form insulated layers of catalysts.

(Catalysts) The catalysts used for this example are cesium salts from phosphoric tungstic acid and are tablet shaped with diameter of 5mm. These catalysts are prepared as follows: mix together 150g (circa 0.0438 mol) of phosphoric tungstic acid reagent sold at store (manufactured by Wako Pharmaceutical) and 60ml of pure water inside a 300ml flask. Dissolve 21.5 (0.110 mol) cesium nitrate (CsNO3) into water, stirring with the aid of a rod, and drop this into the phosphoric tungstic acid solution. As soon as the drops reach the solution, white minuscule crystals of phosphoric tungstic acid cesium salts are separated. Then put the flask into a warm water bath to let the water evaporate. Scoop out the remaining substance onto laboratory dish, then put it into a dryer to dry for six hours at 150 with air. Smash the dried solid into pieces before using machinery to shape them into tablets with diameter of 5mm.

y0021 z(Enforced example 1) Using the reaction device mentioned above, reaction test was performed in each reactor as follows:

(The first reactor) Under the condition of pressure 9.3 atm, mix ethylene, acetic acid, water and inert gas with mol ratio 80.0 : 6.7 : 3.0 : 10.3, flow this mixture at 231g/h to pass through the temperature adjusting unit of the first reactor to be heated up to 158 . The mixture then enters from the top and reacts in the layers of catalysts with a volume of 30cm^3 filled with catalysts prepared as above. The amount of the products, ethyl acetate, at this reactor was 8.8g/h. The temperature at the exit of layers of catalysts was 173 .

y0022 z(The second reactor) The gas mixture flows out of the first reactor and passes through the temperature adjusting unit of the second reactor to be cooled down to 160 . The gas mixture enters from the top and reacts in the layers of catalysts with a volume of 40cm^3 filled with catalysts prepared as above. The amount of the products, ethyl acetate, at this reactor was 11.4g/h. The temperature at the exit of layers of catalysts was 179 .

catalysts of the third reactor with a volume of 40cm^3 filled with catalysts prepared as above. The amount of the products, ethyl acetate, at this reactor was 10.3g/h. The temperature at the exit of layers of catalysts was 179 and pressure at the exit was 8.9 atm.

y0024 zThe overall reaction ratio of addition reaction between ethylene and acetic acid at the insulated reaction apparatus composed with these three reactors indicated the conversion rate of acetic acid being 66.1%. and ethylene's selection ratio to ethyl acetate being 94.3%. The overall SV rate was 1730/h and STY 277g (amount of the products ethyl acetate) / l (amount of catalysts) /h.

y0025 zThe outcome achieved by this example shows that by cooling down the gas mixture whose temperature has beer raised at the previous insulated layers of catalysts at the cooling unit before flowing to the next insulated layers of catalysts. the reaction heat generated during contact reaction was effectively removed at each stage to maintain a fixed range of reaction temperature. thus ethyl acetate was produced with high yield and high efficiency.

y0026 z(Comparison example 1) The following reaction test was performed using the same experiment apparatus an catalysts prepared in the same manner as the enforced example.

(The first reactor) Under the condition of pressure 9.3 atm, mix ethylene, acetic acid, water and inert gas with mol ratio o 80.0 : 6.8 : 3.1 : 10.1, flow this mixture at 238g/h to pass through the temperature adjusting unit of the first reactor to b heated up to 159 . The mixture then enters from the top and reacts in the layers of catalysts with volume of 30cm^3 fille with catalysts prepared as above. The amount of the products, ethyl acetate, at this reactor was 9.1g/h. The temperature a the exit of layers of catalysts was 175 .

(The second reactor) Let the gas mixture flow out of the first reactor and directly enter from the top and react in the secon reactor with the layers of catalysts with a volume of 40cm^3 without being cooled down and keeping the same temperature a the exit of the first reactor. Under such circumstances, the temperature at the exit of the second reactor kept on rising. Whe it eventually reached 226 , the flow of gas mixture was put to a stop and substitution of the layers of catalysts with ine gas was conducted. After being cooled down. the reactor was uncovered to examine the state of catalysts. On the catalys of the second reactor was some separated carbon matter and it was clearly the case of catalyst deterioration. The result this comparison example indicates that uncontrollable reaction could occur if the gas mixture was not appropriately cool down between insulated reactors.

y 0027 z

yThe effect of the invention zThe method of producing ethyl acetate by this invention concerns setting a cooling between two adjacent insulated layers of catalysts which cools down the gas mixture whose temperature has been raised the reaction heat at the previous insulated layers of catalysts. This makes it possible to produce ethyl acetate with h conversion ratio as the temperature of the gas mixture is maintained constantly within a fixed range which also elimina any side reaction that may be caused by temperature rise. At this stage, if the gas mixture is cooled down at the cooling to ensure the temperature rise by the reaction at the following insulated layers of catalysts to stay lower than 30 . predicted uncontrollable reaction can be prevented which in turn improves the conversion ratio to ethyl acetate as wel extending the life of catalysts as separation of carbon matter to the catalysts is also avoided.

y0028 zThe apparatus of producing ethyl acetate by this invention consists of at least two insulated reactors in s containing insulated layers of catalysts which make the gas mixture flow and react, and cooling systems inserted betv gas mixture whose temperature has been raised at the prev

lengthen the life of catalysts. Provided the cooling system can suppress the temperature rise at the exit of the following insulated reactor to be no more than 30 , separation of carbon matter and uncontrollable reaction can be prevented at the relative insulated reactor to produce ethyl acetate efficiently and smoothly. To sum it up, the insulated reactor of this invention not only has simpler structure than the usual shell-tube style reactor to give maximum benefit in terms of low cost for the equipment, it also reduces the maintenance cost dramatically due to its simplicity in filling and changing the catalysts.

y Brief explanation by diagram z

yFigure 1 zShows the process of the enforced example using the method and the production apparatus of this invention to produce ethyl acetate.

y Figure 2 z Shows the process of one of usual methods and production apparatuses to produce ethyl acetate.

y Reference of the symbols z

1... gas mixture

4, 14, 24... insulated layers of catalysts

12, 22... cooling units

REFERENCE 2.

AN - 95-093798/13
XR - API 9551466
XRAM- C95-042757
TI - Prodn. of thyl acetate in high yield - comprises feeding compsn. comprising ethylene and acetic acid to 1st adiabatic reactor contg. hetero-polyacid catalyst, cooling and feeding to 2nd reactor
DC - E17
PA - (SHOW) SHOWA DENKO KK
NP - 1
NC - 1
PN - JP07017907-A 95.01.20 (9513) 6p C07C-069/14
PR - 93.06.29 93JP-159730
AP - 93.06.29 93JP-159730
IC - B01J-027/188 C07B-061/00 C07C-067/05 C07C-069/14
AB - (JP07017907-A)
Prepn. of ethyl acetate (I) by reaction of ethylene (II) with acetic acid (II) in the vapour phase using at least 2 series adiabatic reactors comprises (1) feeding a compsn. (IV) comprising (II) and (III) to a first adiabatic reactor packed with solid catalyst (V) comprising heteropolyacid(s) (VIa) and/or its salt(s) (VIb), (2) cooling the reaction product (VII) (3) feeding (VII) to a second adiabatic reactor packed with (V), and (4) opt. repeating processes (2) and (3).
ADVANTAGE - Heat of reaction may be removed more efficiently and reaction temp. may be controlled precisely. The appts. is constructed more economically and (I) is prepd. in high yield and efficiently. (Dwg.1/2)